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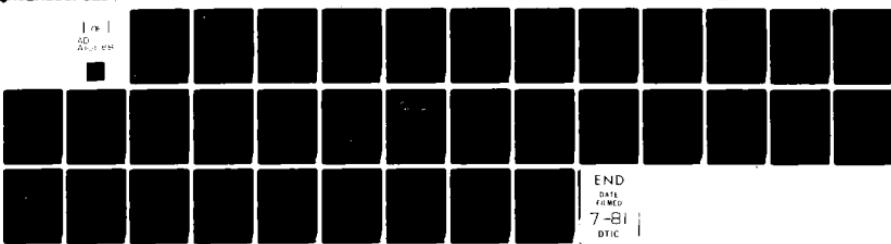
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SYNTHESIS OF NEW INORGANIC AND ORGANOMETALLIC
MATERIALS

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20. Abstract This report describes several research projects in organometallic chemistry. New methods are reported for preparing heteronuclear metal cluster complexes with osmium-platinum, -nickel, -rhodium, and -iron bonds. Reactions between platinum compounds and <u>nido</u> -carbaboranes yield new cage carbaplatinaboranes. The activation of acetylenes by nickel, molybdenum and platinum has been shown to give many novel organometal structures, and the results emphasize the role of dimetal complexes in reactivity patterns. New fluorocarbon complexes of platinum and molybdenum are also described.		

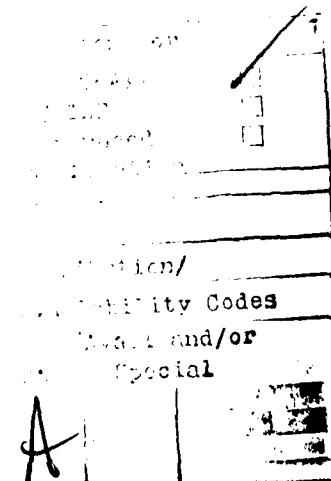
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INTRODUCTION

This report describes research work carried out under Grant Number AFOSR-76-3102 during the period from October 1, 1976 through March 31, 1981. We have previously submitted through the European Office of Aerospace Research three Interim Reports, as well as reprints of various scientific journal articles resulting from work carried out under the Grant.

In addition to the Principal Investigator, the following persons have been associated with the research program for various periods of time during the last 4.5 years. Generally postdoctoral fellows worked with the group for one year or less, whereas graduate students carried out research for longer periods. In the majority of cases stipends for workers were provided by matching funds. Grant funds provided chemicals and other support.

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The project was greatly assisted by collaboration with the X-ray crystallographic group (Drs. J.A.K. Howard and P. Woodward) at Bristol. Additional molecular structure determinations via single-crystal X-ray

* Postdoctoral assistants.

† Graduate students.

diffraction studies were performed by Dr. A.J. Welch initially at Bristol, and subsequently at City University (London). Three senior colleagues (Drs. M. Green, S.A.R. Knox, and J.L. Spencer) assisted with various aspects of the work. A small NATO research grant allowed useful collaboration with Professor T.P. Onak's group at California State University, Los Angeles.

RESEARCH OBJECTIVES.

As described in our original research proposal, the object of our work was to synthesise and to structurally characterise new organometallic compounds which are potentially useful materials. Specific areas for study were: (1) Polynuclear metal structures involving atoms of different elements. This aspect of the work was to include extension of earlier researches on platinacarbaboranes. (2) The activation of acetylenes and olefins by metal complexes, and (3) New chemistry of fluorocarbon complexes of transition metals. We have carried out research in all three areas, but as the project developed emphasis was placed on topics (1) and (2) in view of their increasing interest to chemists, as revealed, for example, in recently held symposia of the American Chemical Society, and in the appearance of many primary journal articles.

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A. D. BLOSE

Technical Information Officer

RESEARCH PROGRESS*

1. POLYNUCLEAR METAL COMPLEXES.

(a) Heteronuclear Cluster Compounds of the Sub-Group VIII Metals.

In our earlier work,[†] on metallacarbaboranes we made the important discovery that low-valent complexes of Ni, Pd, or Pt would add to closo-carbababoranes causing a polyhedral expansion to occur with incorporation of the metal atom into the cage of boron and carbon atoms. In work under the present Grant we have successfully shown that this principle of combining a nucleophilic metal species with an electrophilic system can be used to obtain a variety of heteronuclear metal complexes, thereby providing chemists with a new approach to preparing materials with metal - metal bonds. As a model for our work we selected the 46 electron cluster complex $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ which contains two $\text{Os}(\mu\text{-H})\text{Os}$ three-centre two-electron bonds analogous to those found in boranes.[‡] We studied reactions of the triosmium compound with low valent complexes of Pt, Ni, and Rh.

Reactions between $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ and the compounds $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ [$\text{PR}_3 = \text{P}(\text{cyclo-C}_6\text{H}_{11})_3$, PPh_3 or PBu_2^tMe] afforded tetra-nuclear metal complexes $[\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}(\text{PR}_3)]$.¹⁰ Studies on the

*Reference numbers in the text refer to the Cumulative List of journal articles given on pages 29 - 32.

[†]The work referred to was carried out under AFOSR Grant 71-2090 and was fully described in a Final Report (September 1976) and reviewed by the Principal Investigator (F.G.A. Stone, J. Organomet. Chem., 1975, 100, 257).

[‡]For a discussion of the bonding in this novel triosmium cluster see R.W. Broach and J.M. Williams, Inorg. Chem., 1979, 18, 314.

variable-temperature ^1H n.m.r. spectra of these '58-electron' clusters revealed dynamic behaviour with site-exchange of the two hydrido ligands, the energy barrier for this process being circa 58 kJ mol^{-1} . In order to establish the molecular structure of these complexes a single-crystal X-ray diffraction study was made on the compound containing the $\text{P}(\text{cyclo-C}_6\text{H}_{11})_3$ ligand. The structure is shown in Figure 1. The metal atoms adopt a slightly asymmetric tetrahedral structure [Os - Os 2.777(1), 2.741(1), and 2.789(1) \AA ; Os - Pt 2.791(1), 2.832(1), and 2.863(1) \AA]. The platinum atom is bonded to a CO group and to the $\text{P}(\text{cyclo-C}_6\text{H}_{11})_3$ ligand, and each osmium is attached to three CO groups. The hydrido-ligands bridge the longer of the Os - Os and Os - Pt bonds, as deduced from observation of residual electron densities, from widening of certain Pt - Os - CO and Os - Os - CO angles, from staggered conformations of two of the $\text{Os}(\text{CO})_3$ groups with respect to the two longer edges of the tetrahedron, and from calculation of potential energy minima.

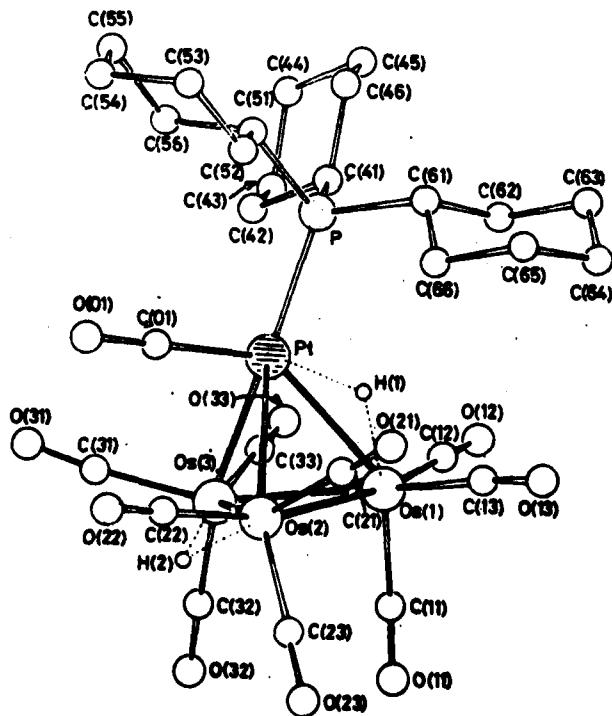


FIGURE 1 Molecular structure of the complex $[\text{Os}_3\text{Pt}(\mu\text{-H})_6(\text{CO})_{10}(\text{P}(\text{cyclo-C}_6\text{H}_{11})_3)]$

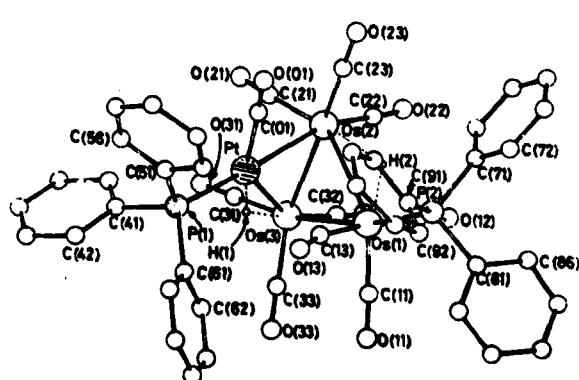
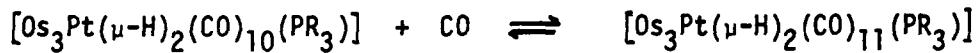


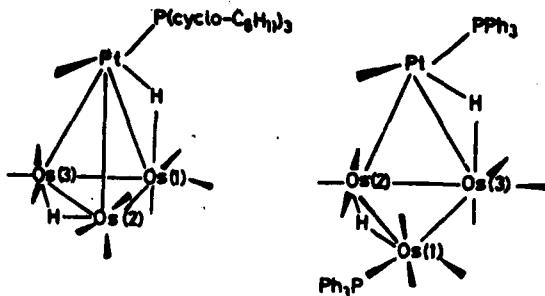
FIGURE 2 Molecular structure of $[\text{Os}_6\text{Pt}(\mu\text{-H})_8(\text{CO})_{16}(\text{PPh}_3)_2]$ showing the crystallographic numbering sequence

It was of interest to investigate reactions of the cluster compounds $[\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}(\text{PR}_3)]$ with donor molecules in order to establish whether 60-electron configurations were attained, and if so, whether or not the closo structure was preserved. Reactions of the Os_3Pt clusters with CO , PPh_3 and AsPh_3 were investigated.¹¹ When CO gas is bubbled through solutions of $[\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$ in diethyl ether, within a few seconds the original green colour of the solution becomes bright yellow. However, when the CO atmosphere is removed the yellow solution acquires a green tinge due to reformation of the starting compound, and establishment of the equilibrium:



Reversible reaction of CO with a metal cluster in this manner is of importance to current interest in catalytic conversion of CO and H_2 into hydrocarbons. It was therefore important to elucidate the structural changes in the metal framework accompanying addition of one or other (CO , PPh_3 or AsPh_3) of the electron pair donors to the 58-electron complexes. Fortunately, suitable crystals of the compound $[\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}(\text{PPh}_3)_2]$ were available for X-ray diffraction study¹¹ and the molecular structure determined in this manner is shown in Figure 2. The four metal atoms adopt a butterfly arrangement in contrast to the tetrahedral cluster structure of the 58-electron precursors $[\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}(\text{PR}_3)]$. In $[\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}(\text{PPh}_3)_2]$ the metal - metal bonding distances are $\text{Os} - \text{Pt}$ 2.717(1) and 2.848(1) \AA and $\text{Os} - \text{Os}$ 2.773(1), 2.914(1) and 3.043(1) \AA . The two hydrido-ligands bridge the longer $\text{Os} - \text{Pt}$ and $\text{Os} - \text{Os}$ bonds. One triphenylphosphine ligand is attached to platinum and the other to osmium, and all the carbonyl ligands are terminally bound.

A comparison of the metal atom framework of the 58 and 60 electron clusters is shown in Figure 3 from which it will be seen that



Comparison of corresponding metal-metal separations
(Å)

Complex	Complex
Pt-Os(1)	2.863(1)
Pt-Os(2)	2.791(1)
Pt-Os(3)	2.832(1)
Os(1)-Os(2)	2.777(1)
Os(1)-Os(3)	2.741(1)
Os(2)-Os(3)	2.789(1)
	2.848(1)
	3.530(1)
	2.717(1)
	2.914(1)
	2.773(1)
	3.043(1)
Pt-Os(3)	Pt-Os(1)
Pt-Os(2)	Pt-Os(3)
Os(1)-Os(3)	Os(1)-Os(2)
Os(2)-Os(3)	Os(2)-Os(3)
Os(1)-Os(2)	Os(1)-Os(2)

FIGURE 3.

addition of a molecule of PPh_3 results in rupturing of a Pt - Os bond, giving rise to a 'butterfly' geometry for the metal atoms.

In contrast with the formation of the 60-electron 'butterfly' cluster shown in Figure 2, with a Os_3Pt core of metal atoms, the corresponding nickel compound was found¹² by single crystal X-ray diffraction to have a closo structure (Figure 4). The compound $[\text{NiOs}_3(\mu-\text{H})_2(\mu-\text{CO})_2(\text{CO})_8(\text{PPh}_3)_2]$ also differed from its platinum analogue by having two bridging CO ligands. It was prepared¹² by reacting $[\text{Ni}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ with $[\text{Os}_3(\mu-\text{H})_2(\text{CO})_{10}]$, a PPh_3 ligand transferring from nickel to osmium in this novel reaction.

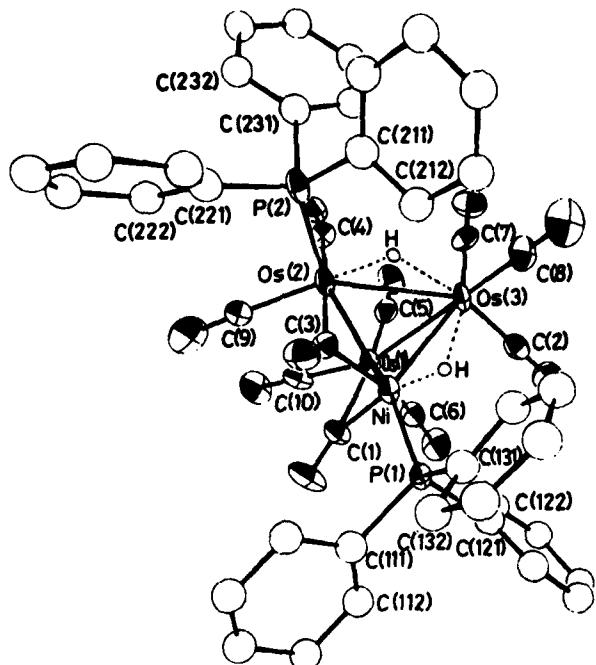


FIGURE 4. Molecular structure of $\cdots [NiOs_4(\mu-H)_8(\mu-CO)_8(CO)_8(PPPh_3)_3]$, showing the crystallographic numbering

The unsaturated triosmium compound $[Os_3(\mu-H)_2(CO)_{10}]$ also reacts with $[Rh(acac)(C_2H_4)_2]$ (acac = acetylacetone) affording the novel cluster complex $[Os_3Rh(\mu-H)_2(acac)(CO)_{10}]$. An X-ray diffraction study¹² showed (Figure 5) that the four metal atoms adopt a 'butterfly' geometry.

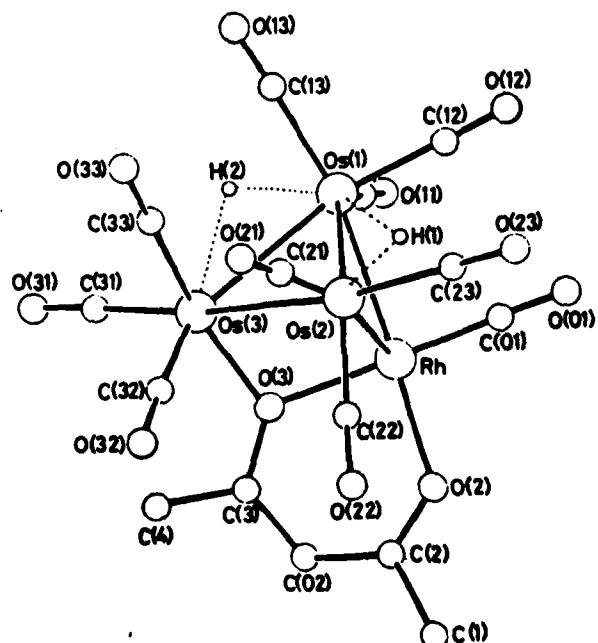


FIGURE 6 Molecular structure of $\left[\text{Os}_3\text{Rh}(\mu\text{-H})_3(\text{acac})_6(\text{CO})_{12}\right]$, showing the crystallographic numbering

The pentane-2,4-dionato-ligand is chelated to the rhodium atom at one extremity but one of its oxygen atoms also bridges to an Os atom forming the other wing-tip of the 'butterfly' so that this Os - Rh separation is $3.292(2)$ Å. The pentane-2,4-dionato group thus functions as a five-electron donor, hence the cluster has 60 valence electrons. Detailed ^1H and ^{31}P n.m.r. studies on all the MOs_3 ($\text{M} = \text{Pt, Ni or Rh}$) clusters are reported elsewhere.¹⁰⁻¹²

The observation that in the reactions of the compound $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ with $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]$ a CO ligand is transferred to platinum suggested a new approach to the synthesis of metal clusters containing platinum and other metals.^{13,14} Thus CO ligand transfer achieves two purposes: creation of a vacant co-ordination site on the substrate molecule to which the nucleophilic platinum atom can bond, and stabilisation of the resulting complex due to creation of a more usual co-ordination arrangement around the 'naked' incoming metal atom. This suggested that numerous platinum-containing heteronuclear metal cluster complexes might be accessible by reacting the compounds $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ or $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PR}_3)_2]$ with homonuclear metal carbonyl species even if the latter are not electron-deficient and are co-ordinatively saturated; transfer of CO to the platinum furthering the process. This idea was tested and proved to be true in experiments involving reactions of the compounds $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ with $[\text{H}_2\text{Os}(\text{CO})_4]$ and with $[\text{Fe}_2(\mu\text{-H})(\mu\text{-CO})_2(\text{CO})_6]^-$, respectively.

The complexes $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PR}_3)]$ react at room temperature with $[\text{H}_2\text{Os}(\text{CO})_4]$ in light petroleum to give in high yield cluster compounds $[\text{Os}_2\text{Pt}_2(\mu\text{-H})_2(\text{CO})_8(\text{PR}_3)_2]$ ($\text{R} = \text{Ph, cyclo-C}_6\text{H}_{11}$, or Me).¹⁴ The molecular structure of the PPh_3 derivative was established by single-crystal X-ray diffraction (Figure 6). The four metal atoms adopt the 'butterfly'

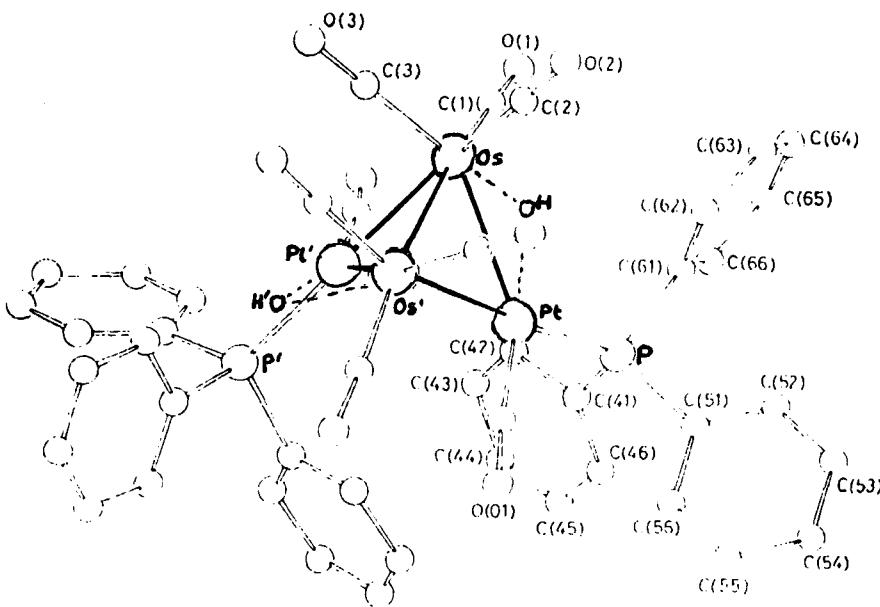


FIGURE 6. Structure of the compound $[\text{Os}_2\text{Pt}_2(\mu\text{-H})_2(\text{CO})_8(\text{PPh}_3)_2]$.

geometry with the two osmium atoms at the 'hinge' [$\text{Os} - \text{Os} = 2.781(4) \text{ \AA}$] and the two platinum atoms at the 'wing-tips' [$\text{Pt} - \text{Pt} = 3.206(0) \text{ \AA}$]. The molecule has two-fold rotational symmetry crystallographically imposed, the two $\text{Os} - \text{Pt}$ distances being $2.862(9)$ and $2.708(9) \text{ \AA}$; the longer bonds are hydrido-bridged.

Tetraethylammonium or bis(triphenylphosphine)iminium salts of the anion $[\text{Fe}_2(\mu\text{-H})(\mu\text{-CO})_2(\text{CO})_6]^-$ react with the complex $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PPh}_3)]$ in tetrahydrofuran to give the diirondiplatinum compounds $[\text{R}] [\text{Fe}_2\text{Pt}_2(\mu\text{-H})(\mu\text{-CO})_3(\text{CO})_5(\text{PPh}_3)_2]$ [$\text{R} = \text{NEt}_4$ or $\text{N}(\text{PPh}_3)_2$].¹³ The structure of the $[\text{N}(\text{PPh}_3)_2]^+$ salt was established by a single-crystal X-ray diffraction study (Figure 7). The $[\text{N}(\text{PPh}_3)_2]^+$ cation is bent [$\angle \text{P} - \text{N} - \text{P} 138.1(8)^\circ$], while the metal framework of the anion consists of a cluster of Fe_2Pt_2 atoms [$\text{Pt} - \text{Pt} 2.966(1)$, $\text{Pt} - \text{Fe} 2.756(2)$, $2.626(2)$, $2.555(2)$, and $2.562(2)$, $\text{Fe} - \text{Fe} 2.522(2)$], arranged such that a Fe_2Pt triangle, edge-bridged by three CO ligands, is capped by

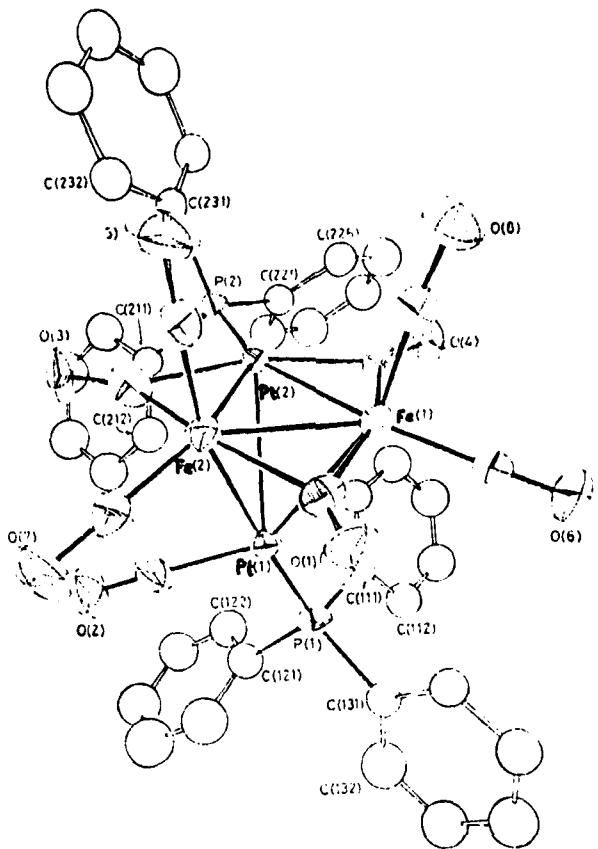


FIGURE 7. Structure of the anion $[\text{Fe}_2\text{Pt}_2(\mu\text{-H})(\mu\text{-CO})_3(\text{CO})_5(\text{PPh}_3)_2]$.

a platinum atom carrying a terminal CO ligand and a PPh_3 group. The four remaining CO ligands are terminally bonded in pairs to the two iron atoms, while the platinum atom in the triangle carries a PPh_3 group. Although not located in the X-ray diffraction study, evidence is presented that the hydrido ligand bridges the longest of the four Fe - Pt separations. Protonation of the salts affords the neutral complex $[\text{Fe}_2\text{Pt}_2(\mu\text{-H})_2(\text{CO})_8(\text{PPh}_3)_2]$, also characterised by an X-ray diffraction study (Figure 8). The structure consists of an Fe_2Pt_2 core [Pt - Pt 2.998(2), Pt - Fe 2.696(3), 2.694(3), 2.631(3) and 2.604(3) \AA], with each iron atom bonded to three CO ligands and each platinum atom to a CO and a PPh_3 group. The hydrido ligands are considered to bridge

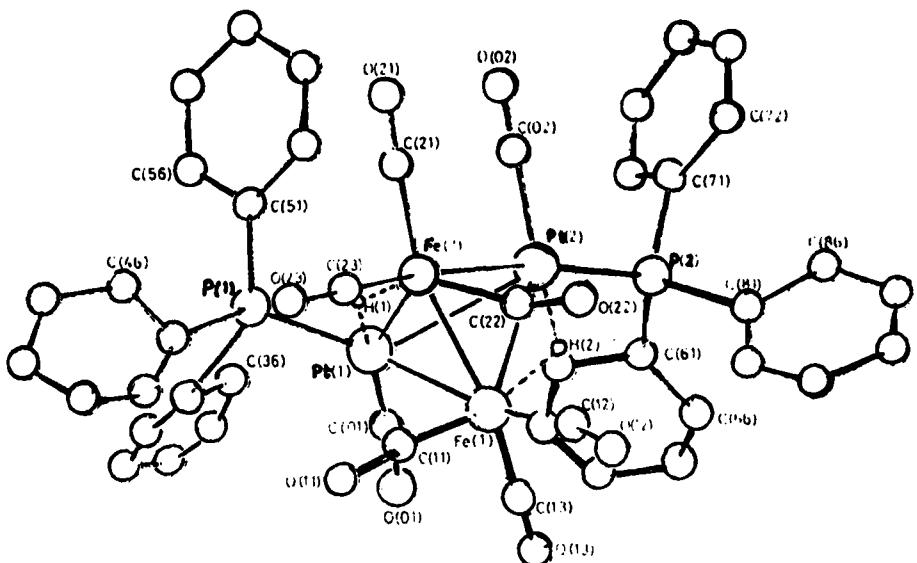


FIGURE 8. Molecular structure of the complex $[\text{Fe}_2\text{Pt}_2(\mu\text{-H})_2(\text{CO})_8(\text{PPh}_3)_2]$

the two longer Fe - Pt edges. The X-ray studies allow an understanding of the ^1H and ^{31}P n.m.r. data for the two Fe_2Pt_2 species, both of which undergo dynamic behaviour in solution (Figure 9).¹³

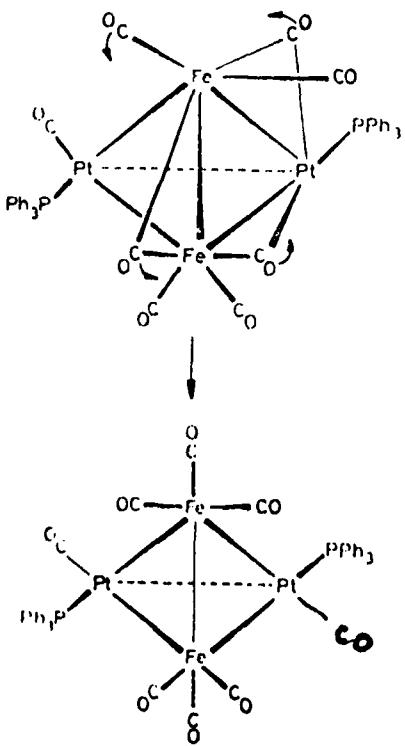


FIGURE 9. Possible mode for conversion of the anion into the metal complex on protonation. Hydrido-ligands are omitted for clarity.

(b) Carbametallaboranes.

We referred earlier (page 3) to our discovery of the direct oxidative - insertion of low - valent metal species into closo-carbaboranes. This work is fully summarised elsewhere.⁶ Briefly the complexes $[\text{Pt}(\text{PET}_3)_3]$, $[\text{Pt}(\text{trans-stilbene})(\text{PR}'_3)_2]$ ($\text{R}' = \text{Et or Me}$), $[\text{M}(\text{cod})(\text{PMe}_3)_2]$ ($\text{M} = \text{Pt or Ni}$; cod = cyclo-octa-1,5-diene), and $[\text{Ni}(\text{cod})(\text{PET}_3)_2]$ react with closo-1,7- R_2 -1,7- $\text{C}_2\text{B}_6\text{H}_6$ ($\text{R} = \text{H or Me}$), closo-4,5- R_2 -4,5- $\text{C}_2\text{B}_7\text{H}_7$, and closo-1,6- $\text{C}_2\text{B}_8\text{H}_{10}$ to give the carbametalla-boranes closo-[4,5- R_2 -6,6-($\text{PR}'_3)_2$ -4,5,6- $\text{C}_2\text{MB}_6\text{H}_6] (M = Pt, R = H, R' = Me;$

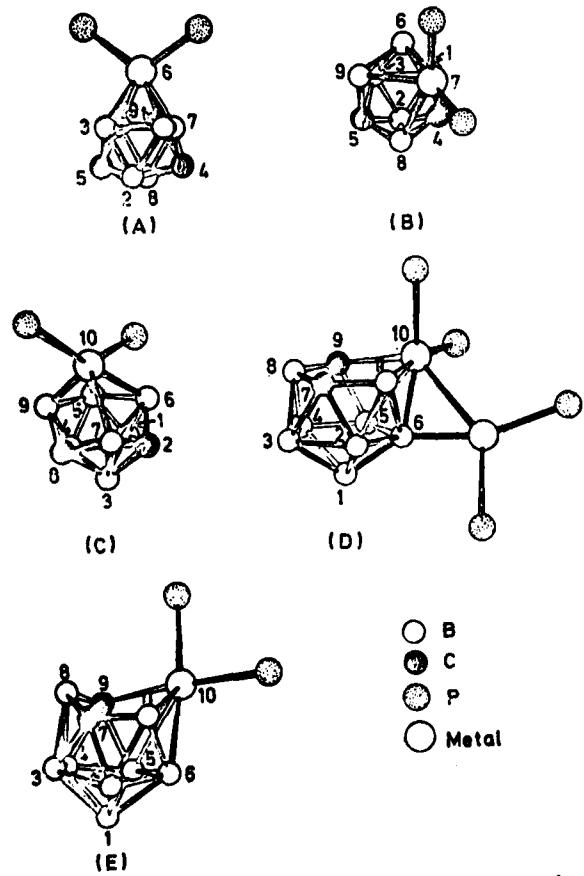


FIGURE 10 Cage-atom arrangements for: (A) closo-complexes ((1), $[\text{6,6-(PMe}_3)_2\text{-4,5,6-C}_2\text{PtB}_6\text{H}_6]$; (3), $[\text{4,5-Me}_2\text{-6,6-(PMe}_3)_2\text{-4,5,6-C}_2\text{PtB}_6\text{H}_6]$; (5), $[\text{4,5-Me}_2\text{-6,6-(PMe}_3)_2\text{-4,5,6-C}_2\text{NiB}_6\text{H}_6]$; and (7), $[\text{4,5-Me}_2\text{-6,6-(PMe}_3)_2\text{-4,5,6-C}_2\text{NbB}_6\text{H}_6]$); (B) nido-complexes ((2), $[\text{7,7-6,6-(PMe}_3)_2\text{-4,5,6-C}_2\text{PtB}_6\text{H}_6]$; and (4), $[\text{4,5-Me}_2\text{-7,7-(PMe}_3)_2\text{-4,5,7-C}_2\text{PtB}_6\text{H}_6]$); (C) arachno-complexes ((8), $[\text{10,10-(PET}_3)_2\text{-4,5,7-C}_2\text{PtB}_6\text{H}_6]$; (9), $[\text{2,8-Me}_2\text{-10,10-(PET}_3)_2\text{-2,8,10-C}_2\text{PtB}_6\text{H}_6]$; (10), $[\text{10,10-(PET}_3)_2\text{-2,8,10-C}_2\text{NiB}_6\text{H}_6]$; and (11), $[\text{2,8-Me}_2\text{-10,10-(PMe}_3)_2\text{-2,8,10-C}_2\text{NbB}_6\text{H}_6]$); (D) ((12), nido- μ -(6,10)- $\{\text{Pt}(\text{PMe}_3)_3\text{-10,10-(PMe}_3)_2\text{-7,9,10-C}_2\text{PtB}_6\text{H}_{10}\})$; and (E) ((13), nido-10,10-($\text{PMe}_3)_2\text{-7,9,10-C}_2\text{PtB}_6\text{H}_{10}\})$

$M = Pt, R = Me, R' = Me$ or $Et; M = Ni, R = Me, R' = Me$ or Et),
nido-[4,5- R_2 -7,7-(PR_3')₂-4,5,7- $C_2PtB_6H_6$] ($R = H, R' = Me$, and $R = Me, R' = Et$), nido-[2,8- R_2 -10,10-(PR_3')₂-2,8,10- $C_2MB_7H_7$] ($M = Pt, R' = Et$, $R = H$ or $Me; M = Ni, R = H, R' = Et$, and $R = Me, R' = Me$), and nido-[μ -(6,10)-{ $Pt(PMe_3)_2$ }-10,10-($PMe_3)_2$ -7,9,10- $C_2PtB_8H_{10}$], respectively.

The latter compound, on reaction with activated charcoal, afforded the compound nido-[10,10-($PMe_3)_2$ -7,9,10- $C_2PtB_8H_{10}$]. The 1H , ^{11}B , and ^{31}P n.m.r. spectra of the new compounds were measured, and their mechanism of formation and molecular structures (Figure 10) established.

Having studied reactions of the closo-carbaboranes we next investigated reactions of Pt^0 complexes with nido-carbaboranes. Reaction of $[Pt_2(\mu\text{-cod})(PEt_3)_4]$ (cod = cyclo-octa-1,5-diene) with 2,3-dicarba-nido-hexaborane(8), 2,3-dimethyl-2,3-dicarba-nido-hexaborane(8), and mono-carba-nido-hexaborane(9) affords respectively,

nido- $\mu_{4,5}$ -{trans-(Et_3P)₂ $Pt(H)$ }- $\mu_{5,6}$ -H-2,3- CB_5H_6],
nido- $\mu_{4,5}$ -{trans-(Et_3P)₂ $Pt(H)$ }- $\mu_{5,6}$ -H-2,3- $C_2B_4H_4$], and
nido- $\mu_{4,5}$ -{trans-(Et_3P)₂ $Pt(H)$ }- $\mu_{3,4}$ -H)($\mu_{5,6}$ -H)-2- CB_5H_6]⁷. The molecular structure of nido- $\mu_{4,5}$ -{trans-(Et_3P)₂ $Pt(H)$ }- $\mu_{5,6}$ -H-2,3- $C_2B_4H_6$ has been established by a single-crystal X-ray diffraction study. The cage core atoms of the molecule maintain a nido pentagonal-pyramidal geometry, with adjacent facial carbon atoms (Figure 11). Both pentagonal B - B links are bridged, one by hydrogen and the other by a trans-(Et_3P)₂ $Pt(H)$ fragment, the latter demonstrating insertion by the metal nucleophile into a bridging B_2H function of the nido-carbaboranes. The 1H , ^{11}B , and ^{31}P n.m.r. spectra of the new compounds were measured and the results are discussed in terms of the molecular structures of the carbaplatinaboranes.⁷

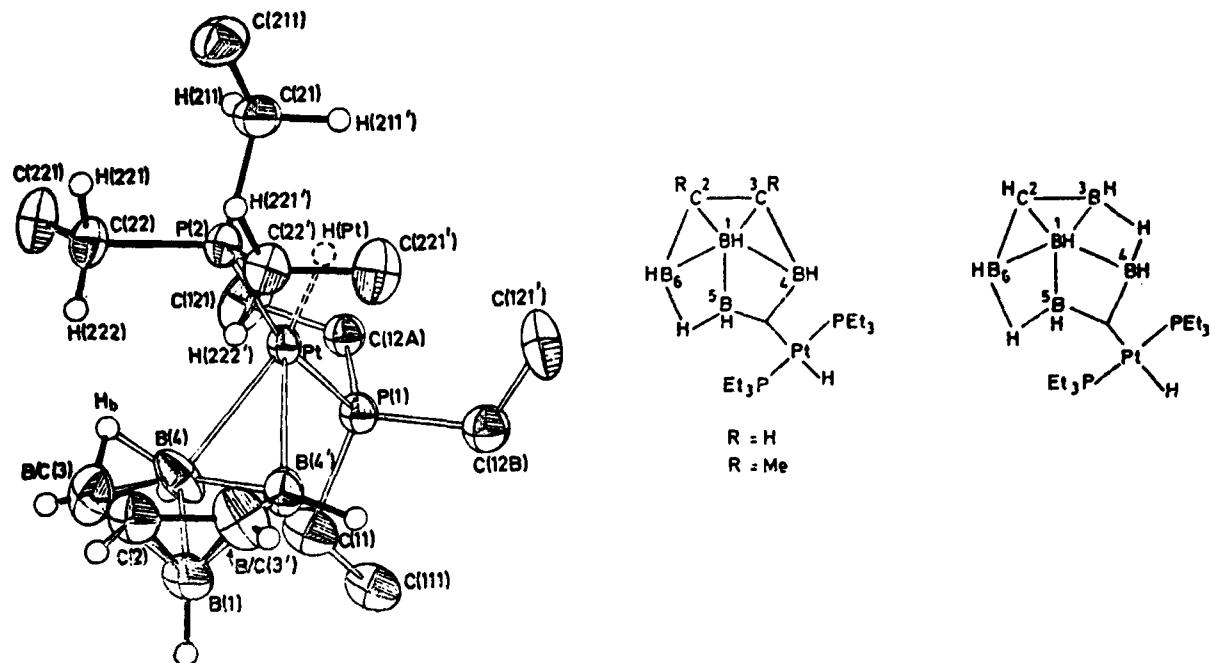


FIGURE 11 The molecule $[nido-14.4.4\text{-}\{trans\text{-}(\text{Et}_3\text{P})_2\text{Pt}(\text{H})\}\text{-}14.4.4\text{-H-2,3-C}_9\text{B}_9\text{H}_4]$ with the numbering used in the crystallographic study. Non-H atom thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have an artificial radius of 0.1 Å for clarity.

Formation of these nido-platinacarbaborane cage structures prompted an investigation of the effect of heat to establish whether loss of hydrogen would occur to afford closo - cage structures. This proved to be so.

Pyrolysis of $[\text{nido-}\mu_{4,5}\text{-}\{\text{trans-}(\text{Et}_3\text{P})_2\text{Pt}(\text{H})\}\text{-}\mu_{5,6}\text{-H-2,3-Me}_2\text{-2,3-C}_2\text{B}_4\text{H}_4]$ affords the closo-carbametallaborane $[\text{1,1-}(\text{Et}_3\text{P})_2\text{-2,3-Me}_2\text{-1,2,3-PtC}_2\text{B}_4\text{H}_4]$, structurally characterised by X-ray diffraction (Figure 12).⁸ The molecules has a highly distorted pentagonal-bipyramidal cage with a novel (C_{2v}) conformation of the $\text{Pt}(\text{PEt}_3)_2$ fragment. In contrast, pyrolysis of $[\text{nido-}\mu_{4,5}\text{-}\{\text{trans-}(\text{Et}_3\text{P})_2\text{Pt}(\text{H})\}\text{-}\mu_{5,6}\text{-H-2,3-C}_2\text{B}_4\text{H}_6]$ proceeds with separation of the cage carbon atoms, affording $[\text{closo-1,1-}(\text{Et}_3\text{P})_2\text{-1,2,4-PtC}_2\text{B}_4\text{H}_6]$.

which may alternatively be prepared directly from $1,6-\text{C}_2\text{B}_4\text{H}_6$ or $5\text{-Me}_3\text{N-2,4-C}_2\text{B}_4\text{H}_6$. The two crystallographically independent molecules in the asymmetric unit (Figure 13) both have pentagonal-bipyramidal cages, but are related as rotational conformers about the metal - cage axis. Comparison of the molecular parameters of the three seven-vertex cages thus studied with those of analogous 12-vertex (icosahedral) systems suggests that the barrier to rotation of a metal fragment, about the axis linking it to the cage, should be less in the former case, and this has been verified by variable-temperature n.m.r. studies.⁸

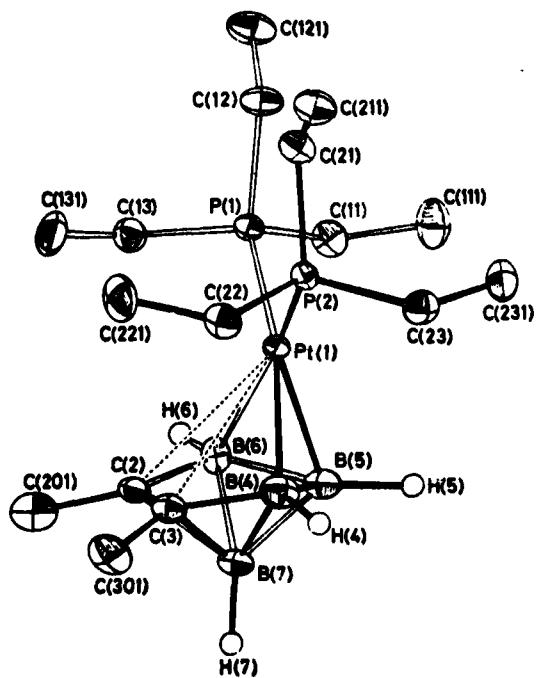


FIGURE 12. Molecular structure of $[1,1-(\text{Et}_3\text{P})_2-2,3\text{-Me}_2-1,2,3\text{-PtC}_2\text{B}_4\text{H}_4]$

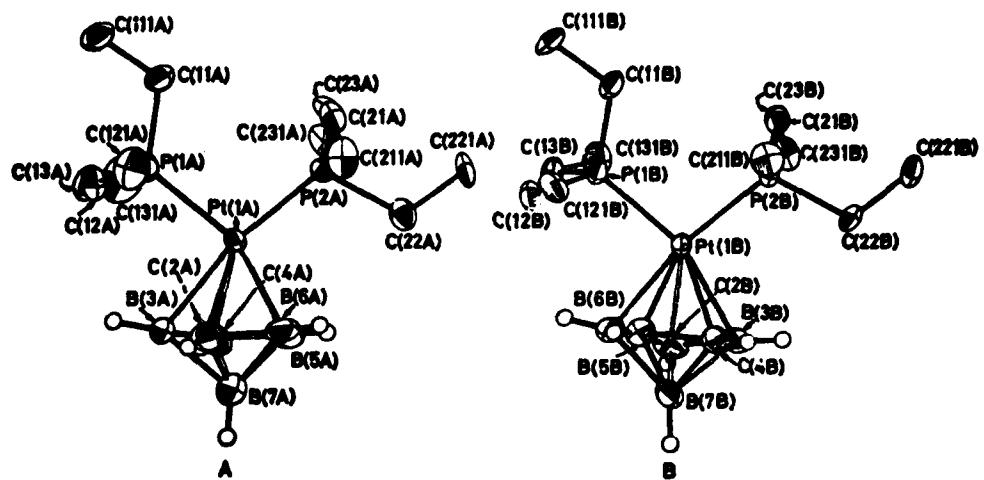
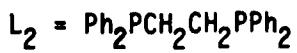
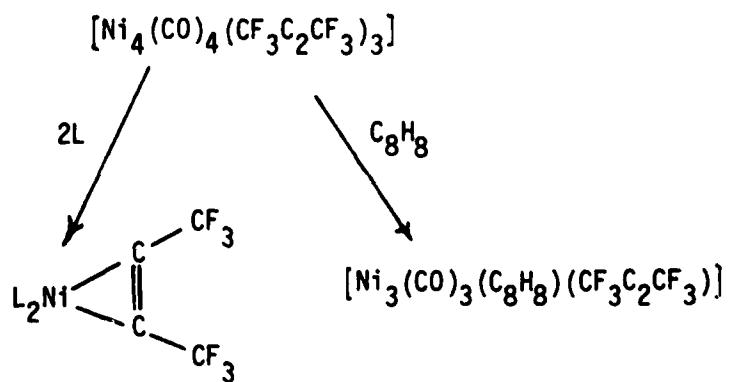


FIGURE 13. Views of the crystallographically independent molecules of
 $[\text{closo-1,1-(Et}_3\text{P)}_2\text{-1,2,4-PtC}_2\text{B}_4\text{H}_6]$.

2. ACTIVATION OF ACETYLENES AND OLEFINS BY METAL COMPLEXES.

(a) Nickel

In the early part of our program we completed our work on the nickel compounds $[\text{Ni}_4(\text{CO})_4\{\mu_3-(n^2-\text{CF}_3\text{C}_2\text{CF}_3)\}_3]$ and $[\text{Ni}_3(\text{CO})_3\{\mu_3-(n^8-\text{C}_8\text{H}_8)\}\{\mu_3-(n^2-\text{CF}_3\text{C}_2\text{CF}_3)\}]$ (Scheme).⁵ The molecular structures were established by single-crystal X-ray diffraction studies (Figures 14 and 15). The structure of the trinickel compound (Figure 15)



Scheme

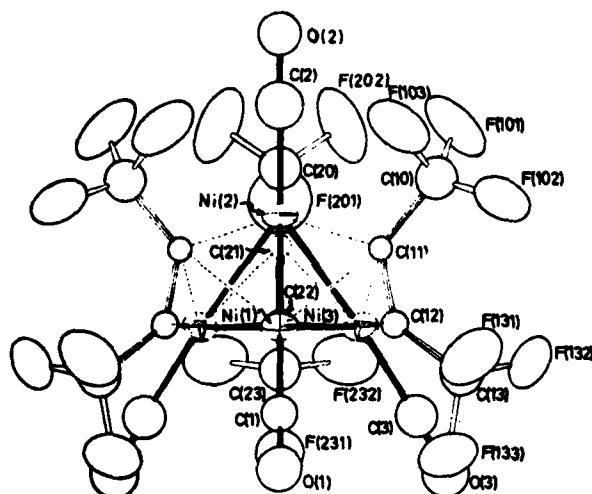


FIGURE 14 View of the complex $[\text{Ni}_4(\text{CO})_8(\mu_3\text{-CF}_3\text{C}_2\text{CF}_3)_4]$

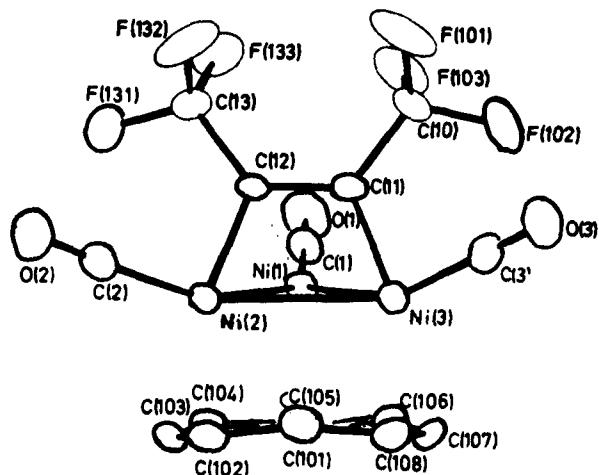


FIGURE 15. Side-on view of the complex $[\text{Ni}_3(\text{CO})_8(\mu_3\text{-CF}_3\text{C}_6\text{F}_5)-(\mu_2\text{-C}_6\text{H}_5)]$ (5). Hydrogen atoms are omitted for clarity.

is especially novel since bond distances within the planar C_8H_8 ring suggests that it is co-ordinated as a 6π electron di-cation $[C_8H_8]^{2+}$. Recently this dication of cyclo-octa-tetraene has been identified via n.m.r. studies using SbF_5/SO_2ClF solutions.* We appear to have stabilised $[C_8H_8]^{2+}$ by complexation with an Ni_3 -triangle. This cyclooctatetraene-trinickel complex was prepared by reacting C_8H_8 with the compound $[Ni_4(CO)_4\{\mu_3-(n^2-CF_3C_2CF_3)\}_3]$, in synthetic work which has demonstrated the ease with which tetranuclear nickel acetylene complexes $[Ni_4L_4\{\mu_3-(n^2-RC_2R)\}_3]$ break down to smaller nickel containing fragments.⁵

(b) Molybdenum

Part of the research on acetylene complexes of molybdenum stemmed from a desire to identify the individual steps in γ -lactone formation from CO and acetylenes, catalysed by transition metal complexes.[†] We have

*G.A. Olah, J.S. Staral, G. Liang, L.A. Pawuette, W.P. Melega, and M. Carmody, J.Am.Chem.Soc., 1977, 99, 3349.

[†] G.P. Chisholm and L. Casser, Angew.Chem.Int.Edn., 1967, 6, 124; P.W. Jolly, and G. Wilke, "The Organic Chemistry of Nickel" Academic Press, 1975, Vol. 2, pp. 322 - 361.

explored⁴ reactions of $[\text{MR}(\text{CO})_3(\text{n-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}$, $\text{R} = \text{COCF}_3$, Me , or PhCH_2 ; $\text{M} = \text{W}$, $\text{R} = \text{COCF}_3$ or Me) with but-2-yne either thermally or on u.v.

irradiation and isolated the crystalline vinylketone complexes

$[\text{M}\{\text{C}(\text{Me})\text{:C}(\text{Me.C(R)O})\text{CO}\}_2(n\text{-C}_5\text{H}_5)]$ ($\text{R} = \text{CF}_3$, Me , or PhCH_2). These complexes react with donor ligands such as CnBu^t , CO , or PPh_3 to form n^3 -allylic lactone complexes of the type

[M{ n^3 -C(Me).C(Me).C(R).C(0).O}(CO)(n -C₅H₅)L] (L = CO, CNBu^t, or PPh₃). The complex where L = CNBu^t and R = Me was structurally identified by single-crystal X-ray diffraction (Figure 16). A further product obtained from the reaction of [Mo(COCF₃)(CO)₃(n -C₅H₅)] with but-2-yne is a purple-red complex [Mo{C(0).(CMe)₄.C(CF₃).O}(CO)(n -C₅H₅)] crystallographically shown (Figure 17) to contain an unusual eight-membered ring structure containing an n^2 -ketenic group. The mechanism of formation of this and of a related tungsten complex is discussed in reference 4.

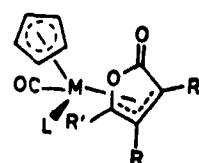
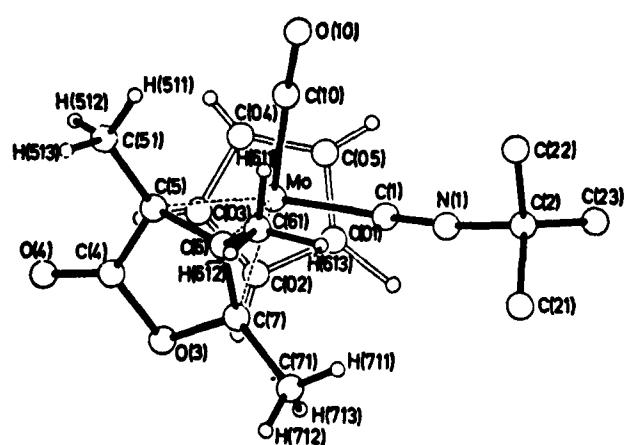


FIGURE 16 The molecular structure of

$$[\text{Mo}(\eta^3\text{-C}(\text{Me})\text{-C}(\text{Me})\text{-C}(\text{Me})\text{-C}(\text{O})\text{-O})(\text{CO})(\eta\text{-C}_5\text{H}_5)(\text{CNBu}^t)]$$

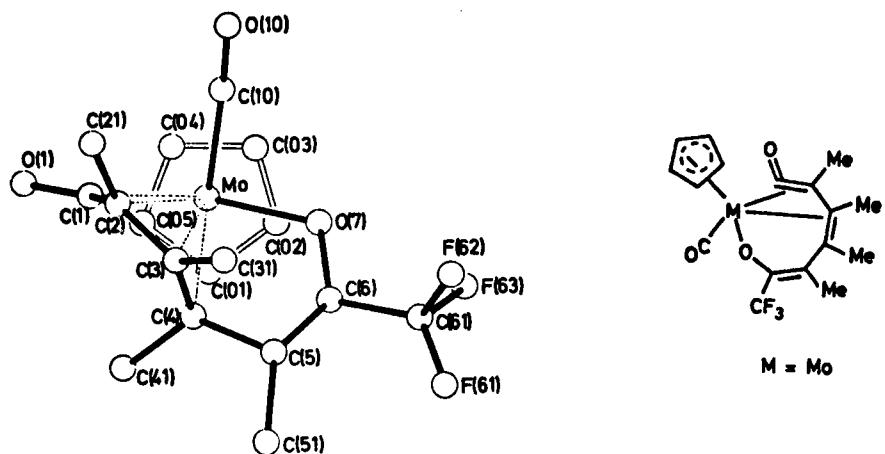
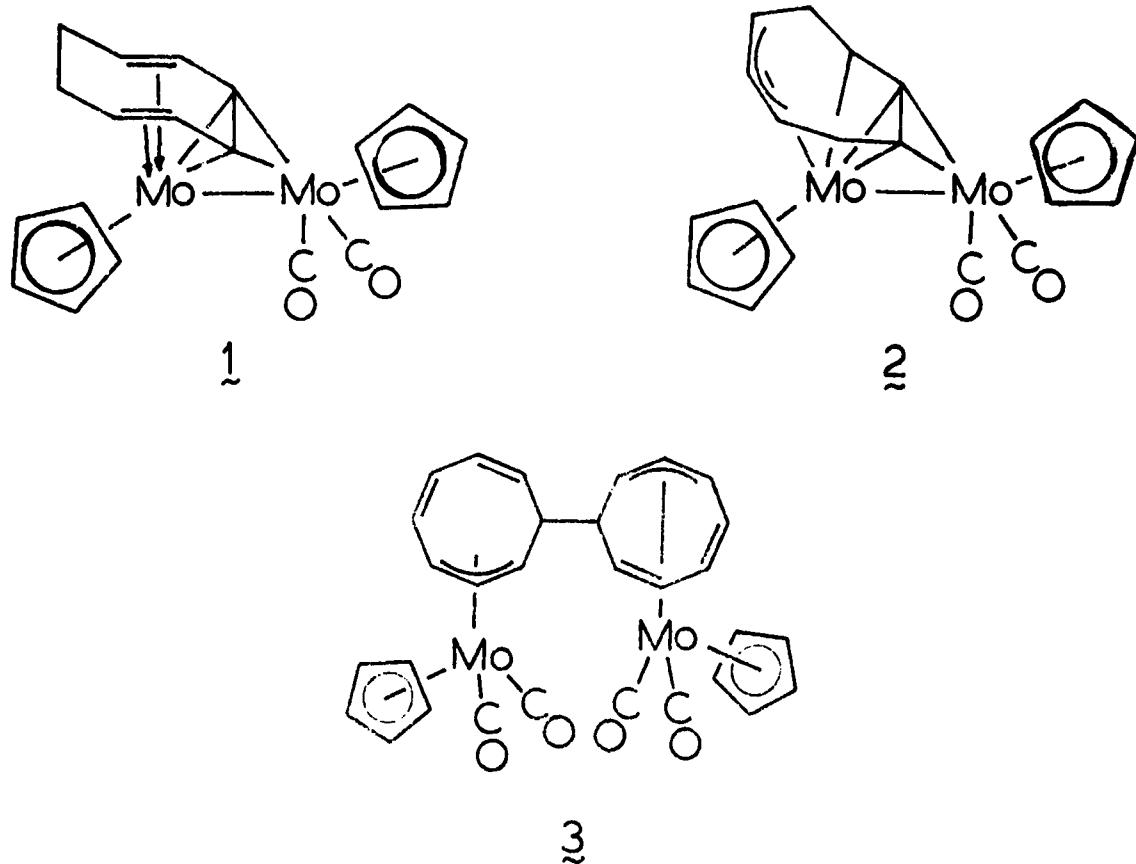


FIGURE 17 The molecular structure of
 $[\text{Mo}(\text{C}(\text{O})\text{-C}(\text{Me})\text{-C}(\text{F}_3)\text{-O})(\text{CO})(\eta\text{-C}_5\text{H}_5)]^{2+}$

We have directed much of our research effort to demonstrating the reactivity of dimetal centres in complexes. Hitherto the reactivity of acetylenes, olefins, dienes, etc in transition metal chemistry has been associated with co-ordination of these species to a single metal atom in a complex. We have been able to demonstrate the important role that can be played by two metal centres interacting together with an unsaturated hydrocarbon.

Reaction of the dimolybdenum compounds $[\text{Mo}_2(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$ or $[\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ with cyclo-octatetraene in octane or heptane at reflux affords a complex mixture from which the species $[\text{Mo}_2(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2(\text{C}_8\text{H}_8)]$ (1) and $[\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2(\text{n}^3\text{-C}_16\text{H}_{16})]$ (3) were isolated and characterised.¹⁵ The maroon complex $[\text{Mo}_2(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2(\text{C}_8\text{H}_8)]$ (1) is stable in non-polar solvents but in polar solvents such as acetone, chloroform, or acetonitrile it transforms to an orange isomer (2). Carbon-13 n.m.r. spectroscopy revealed that (1) possessed mirror symmetry, in contrast to (2), and that in both isomers two carbons of the C_8H_8 ligands did not bear protons. The unprecedented rearrangement of cyclo-octatetraene at a Mo_2 centre and

subsequent isomerisation were established by single-crystal X-ray diffraction studies on the two isomeric forms, (1) and (2), of $[\text{Mo}_2(\text{CO})_2(n\text{-C}_5\text{H}_5)_2(\text{C}_8\text{H}_8)]$.

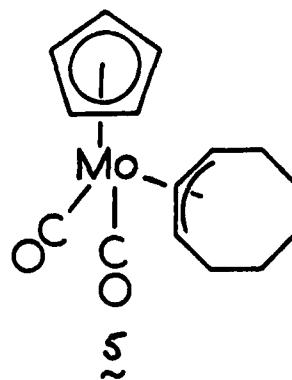
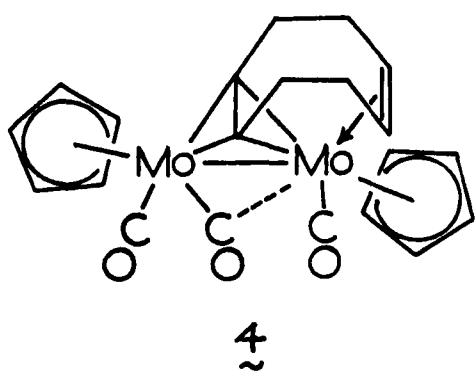


The two isomers differ strikingly in the mode of attachment of the C_8 ring. In both isomers there is n^2 attachment to the $\text{Mo}(\text{CO})_2(n\text{-C}_5\text{H}_5)$ moiety, and an n^6 attachment to the other Mo atom through six contiguous carbon atoms of the C_8 ring, the two common carbon atoms being in the form of a symmetrical transverse acetylenic bridge. In isomer (1) the two carbon atoms on either side of the transverse bridge form two π -ethylenic links to the metal atom, whereas in isomer (2) only one carbon atom forms a σ bond on one side of the bridge, and three carbon atoms form a π -allylic attachment on the other side. The remaining two methylenic

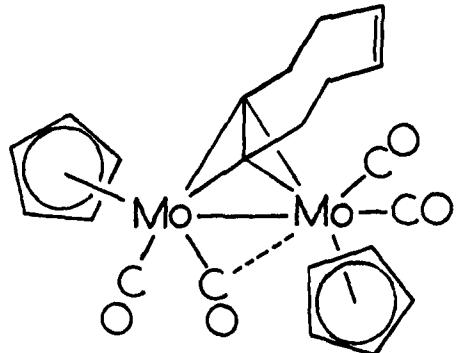
carbon atoms bend away from the n^6 part of the C_8 ring, which is approximately planar, but in crystals of (1) there is a slight twist which destroys the mirror symmetry of the molecule as a whole. In (2) the entire attachment is asymmetric.

Detailed n.m.r. and deuteration studies described elsewhere¹⁵ provide evidence for the mechanisms of formation of (1) and its isomerisation to (2).

In boiling octane, cyclo-octa-1,5-diene and $[\text{Mo}_2(\text{CO})_6(n\text{-C}_5\text{H}_5)_2]$ react to give the compounds $[\text{Mo}_2(\text{CO})_3(n\text{-C}_8\text{H}_{10})(n\text{-C}_5\text{H}_5)_2]$ (4) and $[\text{Mo}(\text{CO})_2(n^3\text{-C}_8\text{H}_{13})(n\text{-C}_5\text{H}_5)]$ (5).¹⁶ An X-ray diffraction study has been carried out on the dimolybdenum species. The alkyne group of a cyclo-octa-1-en-5-yne ligand forms a symmetrical transverse bridge across a molybdenum - molybdenum single bond [$2.986(1) \text{ \AA}^0$], with the ring adopting a 'tub' conformation, concave to the metal - metal bond. This allows the alkene group to form a second ring-to-metal attachment involving only one of the metal atoms. This metal atom also carries one cyclopentadienyl group and one terminal carbonyl ligand. The other metal atom carries one cyclopentadienyl group and two carbonyl ligands, one of which, however, shows the characteristic geometry of a 'weakly semibridging' carbonyl ($\text{Mo} - \text{C}$, 1.94 and 2.98 \AA^0 ; $\text{Mo} - \text{Mo} - \text{C}$, 68^0 ; $\text{Mo} - \text{C} - \text{O}$, 170^0). The molecule possesses no symmetry; the C_8 ring is twisted so that the alkene



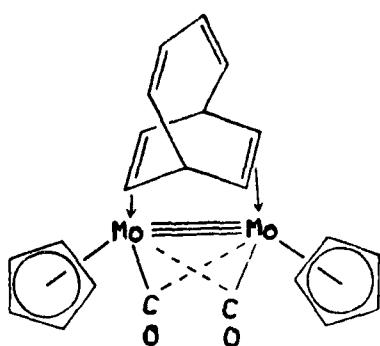
and alkyne moieties are not parallel to one another, and the other ligands are not symmetrically related to the metal - metal bond. The i.r. spectrum of the compound in solution indicates the existence of isomers. However, the ^1H and ^{13}C n.m.r. spectra are invariant down to -80°C and therefore the isomers are interconverting sufficiently rapidly to provide averaged nuclear environments on the n.m.r. time scale, although the nature of the spectra reveal the species present to lack symmetry. It is proposed that rotamers exist, produced by rotation of the $\text{Mo}(\text{CO})_2(\text{n-C}_5\text{H}_5)$ group about an axis through the centrepoint of the μ -alkyne bond, with low barriers to their interconversion. The compound $[\text{Mo}_2(\text{CO})_3(\mu\text{-C}_8\text{H}_{10})(\text{n-C}_5\text{H}_5)_2]$ reacts with CO to give $[\text{Mo}_2(\text{CO})_4(\mu\text{-C}_8\text{H}_{10})(\text{n-C}_5\text{H}_5)_2]$ (6), which shows dynamic n.m.r. properties similar to other $[\text{Mo}_2(\text{CO})_4(\mu\text{-alkyne})(\text{n-C}_5\text{H}_5)_2]$ species.¹⁶



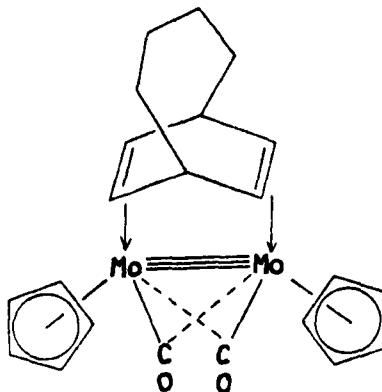
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In a third research project with Mo_2 compounds, the complex $[\text{Mo}_2(\text{CO})_4(\mu\text{-HC}_2\text{H})(\text{n-C}_5\text{H}_5)_2]$ was found to react in octane reflux with cyclo-octatetraene, cyclohexa-1,3-diene, cyclo-heptatriene, and cyclo-octa-1,3-diene to afford dimolybdenum compounds having the bridging bicyclic ligands $\text{C}_{10}\text{H}_{10}$, C_8H_{10} , C_9H_{10} and $\text{C}_{10}\text{H}_{14}$, respectively, formed by formal Diels-Alder 1,4-addition of the diene to the $\text{Mo}_2(\mu\text{-HC}_2\text{H})$ moiety.¹⁷

The molecular structure of the product (7) from cyclo-octatetraene was established by an X-ray diffraction study. A bicyclo[4.2.2]deca-2,4,7,9-tetraene ligand bridges a molybdenum - molybdenum triple bond [$2.504(1) \text{ \AA}^0$] with the double bonds at positions 7 and 9 each co-ordinated to a molybdenum atom. The two carbonyl ligands asymmetrically bridge the metal - metal

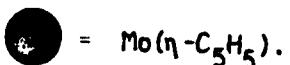
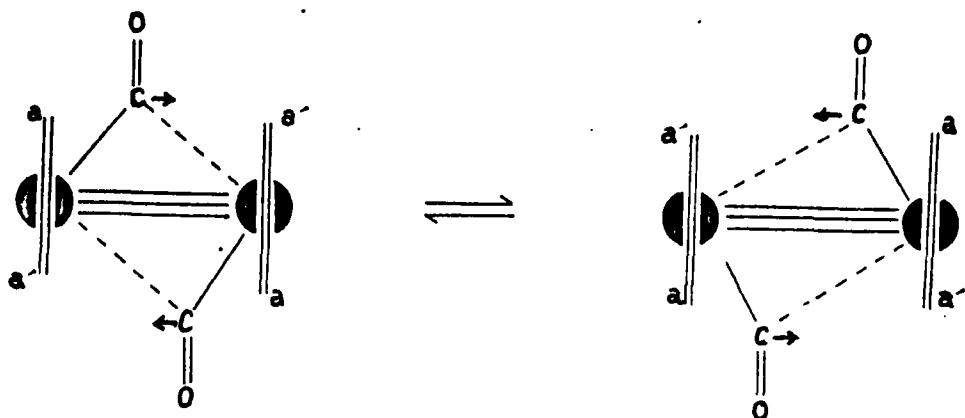


(7)



(8)

bond [mean $\text{Mo} - \text{C} = \text{O}$ 1.99 and 2.33 \AA^0]. The axis of the molecule through the metal - metal bond and the centroids of the $n\text{-C}_5\text{H}_5$ ligands is non-linear, with the two rings in a cis relationship. Hydrogen-1 and ^{13}C n.m.r. data for the complexes are reported and discussed elsewhere.¹⁷ Variable temperature ^{13}C n.m.r. studies on the product (8) from cyclo-octa-1,3-diene revealed dynamic behaviour involving site exchange of the semi-bridging CO ligands (ΔG^\ddagger circa 47 kJ mol^{-1}) (see Scheme, p 24).



Scheme. Site exchange of co-ordinated carbon atoms in bridge system of the dimolybdenum complexes. Only metal-bonded carbon atoms are shown for clarity.

(c) Platinum

Although acetylene complexes of platinum have been known for many years these compounds have been restricted to those containing one platinum atom per molecule. We have developed a synthesis of alkyne - platinum complexes containing two or three metal atoms held together by acetylene molecules transversely bridging the metal - metal vectors.

Reaction of the compound $[\text{Pt}(\text{PhC}_2\text{Ph})_2]$ with $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ or $[\text{Pt}_2(\mu\text{-cod})(\text{PET}_3)_4]$ (cod = cyclo-octa-1,5-diene) affords diplatinum complexes $[\text{Pt}_2(\mu\text{-PhC}_2\text{Ph})(\text{PhC}_2\text{Ph})(\text{PR}_3)_2]$ (R = Ph or Et). The triphenylphosphine compound has also been prepared by treating $\text{PhC}\equiv\text{CPh}$ with $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PPh}_3)_2]$. The terminal alkyne ligand in $[\text{Pt}_2(\mu\text{-PhC}_2\text{Ph})(\text{PhC}_2\text{Ph})(\text{PPh}_3)_2]$ bonds a third platinum atom on treatment with $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ to give the triplatinum

complex $[\text{Pt}_3(\mu\text{-PhC}_2\text{Ph})_2(\text{PPh}_3)_4]$. The latter can also be prepared by addition of 2 mol equivalents of $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ to $[\text{Pt}(\text{PhC}_2\text{Ph})_2]$, and the triethylphosphine-triplatinum analogue is similarly obtained using $[\text{Pt}_2(\mu\text{-cod})(\text{PEt}_3)_4]$.⁹ In view of the novelty of these compounds, a single-crystal X-ray diffraction study has been carried out on $[\text{Pt}_3(\mu\text{-PhC}_2\text{Ph})_2(\text{PEt}_3)_4]$. The three platinum atoms adopt an open V-shaped configuration (Figure 18) with an internuclear distance of 2.90 Å and an interbond angle of 144°, while the acetylenic units form transverse bridges across the two Pt - Pt vectors on the convex side of the V. The phenyl groups bend away from the metal atoms to give a C - C - Ph angle of 139°, and the whole molecule is constrained crystallographically to C_2 symmetry. The ethyl groups of the phosphine ligands are ill defined and possibly disordered

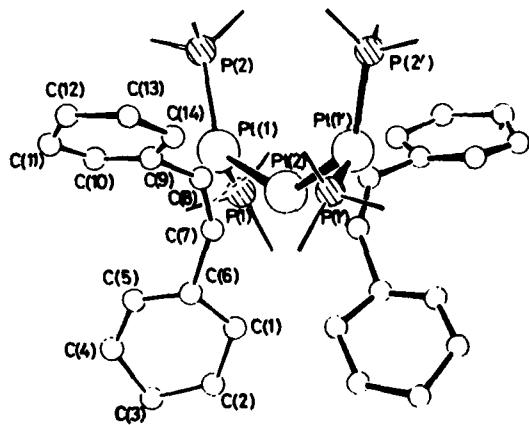
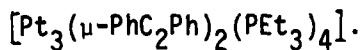


FIGURE 18. Molecular structure of the complex



The diplatinum complexes $[\text{Pt}_2(\mu\text{-RC}_2\text{R})(\text{PMe}_3)_4]$ ($\text{R} = \text{Ph}$ or C_6F_5) have also been prepared, and $[\text{Pt}_2(\mu\text{-PhC}_2\text{Ph})(\text{PEt}_3)_4]$ characterised spectroscopically. Reaction of $[\text{Pt}(\text{PhC}_2\text{Ph})(\text{CNBu}^t)_2]$ with $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ yields trans- $[\text{Pt}_2(\mu\text{-PhC}_2\text{Ph})(\text{CNBu}^t)_2(\text{PPh}_3)_2]$, scrambling of the CNBu^t and PPh_3 ligands having occurred. The stereochemistry of this complex, and its

$\text{PhC}\equiv\text{CC}_6\text{H}_4\text{OMe}-4$ analogue, has been established by ^{31}P and ^{13}C -labelling n.m.r. studies. The modes of formation of the various compounds are discussed elsewhere.⁹

3. FLUOROCARBON COMPLEXES

Studies on fluorocarbon complexes of transition metals provide useful model systems for increasing our understanding of the bonding of organic molecules to metal atoms. In research supported by a previous Grant (AFOSR 71-2090), we prepared and characterised numerous new fluorocarbon-metal compounds as a means of adding to our knowledge of the activation of small molecules by low valent metal atoms. We have continued some work in this area under Grant AFOSR-76-3102, but at a reduced level because of the major progress made with projects described earlier (Sections 1 and 2 of this Report).

Reaction of bis(*n*-cyclo-octa-1,5-diene)platinum with C_2F_4 gives an octafluorodiplatinacyclohexane complex $[\text{Pt}_2(\mu\text{-CF}_2\text{CF}_2)_2(1,5\text{-C}_8\text{H}_{12})_2]$, which undergoes ligand-displacement reactions to form $[\text{Pt}_2(\mu\text{-CF}_2\text{CF}_2)_2\text{L}_4]$ ($\text{L} = \text{PET}_3$; $\text{L}_2 = 1,2\text{-C}_6\text{H}_4(\text{AsMe}_2)_2$).² Tris(*n*-bicyclo[2.2.1]heptene)platinum reacts with C_2F_4 to give the mononuclear species $[\text{Pt}(\text{CF}_2\text{CF}_2)(\text{C}_7\text{H}_{10})_2]$, which with $\text{P}(\text{OMe})_3$ and with $1,5\text{-C}_8\text{H}_{12}$ forms, respectively, $[\text{Pt}(\text{CF}_2\text{CF}_2)\{\text{P}(\text{OMe})_3\}_2]$ and $[\text{Pt}_2(\mu\text{-CF}_2\text{CF}_2)_2(1,5\text{-C}_8\text{H}_{12})_2]$. In contrast $[\text{Pd}(1,5\text{-C}_8\text{H}_{12})_2]$ and C_2F_4 afford the four-ring system $[(1,5\text{-C}_8\text{H}_{12})\text{Pd}(\text{CF}_2\text{CF}_2)\text{Pd}(1,5\text{-C}_8\text{H}_{12})]$. Hexafluoropropene rearranges on treatment with $[\text{M}(1,5\text{-C}_8\text{H}_{12})_2]$ ($\text{M} = \text{Pt}$ or Pd) to form $[(1,5\text{-C}_8\text{H}_{12})\text{M}\{\text{C}(\text{CF}_3)_2\}\text{M}(1,5\text{-C}_8\text{H}_{12})]$. In the case of the palladium system, the complex $[\text{Pd}(\text{CF}_2\text{CF}(\text{CF}_3))(\text{C}_8\text{H}_{12})]$ has also been isolated, and shown to be the precursor of the binuclear complex. Octafluorobut-2-ene, hexafluoroacetone, and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene react with

$[\text{Pd}(1,5\text{-C}_8\text{H}_{12})_2]$ to give the products $[\text{Pd}\{\text{CF}(\text{CF}_3)\cdot\text{CF}(\text{CF}_3)\}(1,5\text{-C}_8\text{H}_{12})]$, $[\text{Pd}\{\text{C}(\text{CF}_3)_2\cdot\text{O}\}(1,5\text{-C}_8\text{H}_{12})]$, and $[\text{Pd}\{\text{C}(\text{CN})_2\cdot\text{C}(\text{CF}_3)_2\}(1,5\text{-C}_8\text{H}_{12})]$.²

The 16-electron chloro-complexes $[\text{MC}_1(\text{CF}_3\text{C}_2\text{CF}_3)_2(n\text{-C}_5\text{H}_5)]$ ($\text{M} = \text{Mo}$ or W) react with TlSC_6F_5 to give compounds $[\text{M}(\text{SC}_6\text{F}_5)(\text{CF}_3\text{C}_2\text{CF}_3)_2(n\text{-C}_5\text{H}_5)]$; the related species $[\text{M}(\text{SC}_6\text{F}_5)(\text{CO})(\text{PhC}_2\text{Ph})(n\text{-C}_5\text{H}_5)]$ were similarly obtained from $[\text{MC}_1(\text{CO})(\text{PhC}_2\text{Ph})(n\text{-C}_5\text{H}_5)]$.¹ Cyclopentadienylthallium reacts with the compounds $[\text{MC}_1(\text{CF}_3\text{C}_2\text{CF}_3)_2(n\text{-C}_5\text{H}_5)]$ to afford insertion products $[\text{MC}(\text{CF}_3)\text{C}(\text{CF}_3)\text{C}_5\text{H}_5(\text{CF}_3\text{C}_2\text{CF}_3)(n\text{-C}_5\text{H}_5)]$, the molybdenum compound being characterised by a single-crystal X-ray diffraction study (Figure 19).

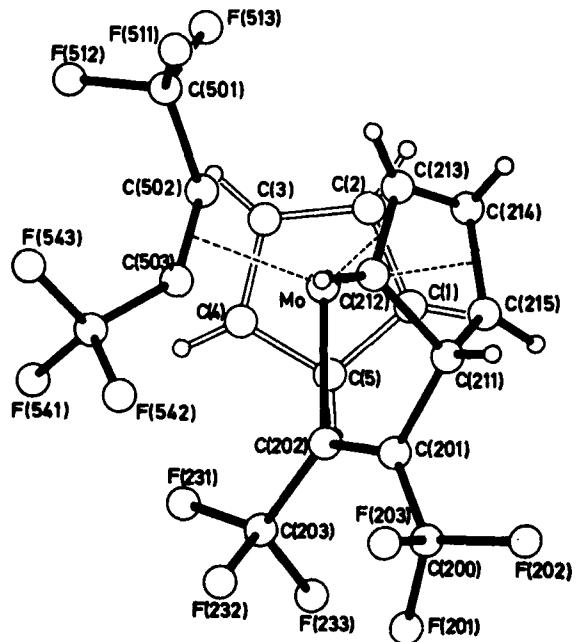


FIGURE 19 $[\text{MoC}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{C}_5\text{H}_5(\text{CF}_3\text{C}_2\text{CF}_3)(n\text{-C}_5\text{H}_5)]$: single molecule viewed normal to the $(n\text{-C}_5\text{H}_5)$ ring.

The molybdenum compound $[\text{MoC}_1(\text{CF}_3\text{C}_2\text{CF}_3)_2(n\text{-C}_5\text{H}_5)]$ undergoes an unusual reaction with the tris(pyrazolyl)borate anion to give a complex containing no boron but an n^3 -allyl group, linking two pyrazole ligands and formed by condensation of the two hexafluorobut-2-yne ligands originally co-ordinated to the metal. Buta-1,3-diene reacts with $[\text{MoC}_1(\text{CF}_3\text{C}_2\text{CF}_3)_2(n\text{-C}_5\text{H}_5)]$ to give

$[\text{MoCl}_2(\eta^4\text{-C}_4\text{H}_6)(\eta\text{-C}_5\text{H}_5)]$ and with $[\text{MoCl}(\text{CO})(\text{PhC}_2\text{Ph})(\eta\text{-C}_5\text{H}_5)]$ to yield the same compound or $[\text{MoCl}(\text{CO})(\eta^4\text{-C}_4\text{H}_6)(\eta\text{-C}_5\text{H}_5)]$, depending on the solvent.

ACCOMPLISHMENTS

During the 4-5 years the Grant has been in operation we have made several significant discoveries in the area of organometallic chemistry. Among the more important results are the following.

- (a) New synthetic methods for obtaining polynuclear metal compounds with heteronuclear metal - metal bonds, e.g. species with Os - Pt, Os - Ni, Os - Rh, and Fe - Pt bonds.
- (b) Oxidative addition of Pt^0 compounds to nido-carboranes to give nido cage compounds which on subsequent pyrolysis afford closo-platinacarboranes
- (c) The discovery of the first metal cluster compound with a planar cyclo-octa-tetraene ring co-ordinated to three nickel atoms.
- (d) Experimental demonstration of the high reactivity of the dimolybdenum complex $[\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ towards cyclo-octa-tetraene, cyclo-octa-1,5-diene, and other dienes. This work has pointed the way to new chemistry at dimetal centres.
- (e) The discovery of di- and tri-platinum complexes with bridging acetylene ligands; in particular the step-wise synthesis of these compounds from monoplatinum acetylene compounds.

CUMULATIVE LIST OF JOURNAL ARTICLES UNDER GRANT AFOSR - 76 - 3102.

1. **Syntheses Involving Co-ordinatively Unsaturated Cyclopentadienyl-molybdenum and -tungsten Complexes. Molecular and Crystal Structures of $[\text{Mo.C(CF}_3\text{)}\text{:C(CF}_3\text{)}\text{.C}_5\text{H}_5\text{(CF}_3\text{C}_2\text{CF}_3\text{)}\text{(n-C}_5\text{H}_5\text{)}]$.**
by J.L. Davidson, M. Green, F.G.A. Stone, and A.J. Welch,
J.Chem.Soc., Dalton Trans., 1977, 287.
2. **Reactions of Low-valent Metal Complexes with Fluorocarbons. Bis(n-cyclo-octa-1,5-diene)-platinum and -palladium with Fluoroolefins.**
by M. Green, A. Laguna, J.L. Spencer, and F.G.A. Stone,
J.Chem.Soc., Dalton Trans., 1977, 1010.
3. **The Reaction of Bis(triethylphosphine)platinum and Pentakis(t-butyl isocyanide)ruthenium with Dicarba-nido-hexaboranes (8): Molecular Structures of $[\text{nido-}\mu_{4,5}\text{-}\{\text{trans-}(\text{Et}_3\text{P})_2\text{Pt(H)}\}\mu_{5,6}\text{-H-2,3-C}_2\text{B}_4\text{H}_6]$, $[\text{closo-1,1-(Et}_3\text{P})_2\text{-2,3-Me}_2\text{-1,2,3-PtC}_2\text{B}_4\text{H}_4]$ and $[\text{RuH(Bu}^t\text{NC)}_5]$ $[\text{nido-2,3-Me}_2\text{-2,3-C}_2\text{B}_4\text{H}_5]$.**
by G.K. Barker, M. Green, T.P. Onak, F.G.A. Stone, C.B. Ungermann, and A.J. Welch, J.Chem.Soc., Chem.Commun., 1978, 169.
4. **Formation of n^3 -Bonded Lactone Complexes and Eight-membered Ring Metallacycles with Ketene Groups by the Insertion of Acetylenes into Carbon-Molybdenum and -Tungsten σ -Bonds; Molecular and Crystal Structures of Carbonyl(n-cyclopentadienyl)(3-5-n-2,3-dihydro-3,4,5-trimethyl-2-oxo-3-furyl)(t-butyl isocyanide)molybdenum and Carbonyl-(n-cyclopentadienyl)(3-4:5-6-n-2,3,4,5-tetramethyl-6-oxo-1-trifluoromethylhexa-1,3,5-trienyloxo)molybdenum.**
by M. Green, J.Z. Nyathi, C. Scott, F.G.A. Stone, A.J. Welch, and P. Woodward, J.Chem.Soc., Dalton trans., 1978, 1067.

5. Formation of Tetra- and Tri-nuclear Nickel Acetylene Complexes; Crystal and Molecular Structures of $[\text{Ni}_4(\text{CO})_4\{\mu_3-(\text{n}^2-\text{CF}_3\text{C}_2\text{CF}_3)\}_3]$ and $[\text{Ni}_3(\text{CO})_3\{\mu_3-(\text{n}^8-\text{C}_8\text{H}_8)\}\{\mu_3-(\text{n}^2-\text{CF}_3\text{C}_2\text{CF}_3)\}]$ with Evidence for a Nickel Stabilised Cyclo-octa-tetraene Dication.
by J.L. Davidson, M. Green, F.G.A. Stone, and A.J. Welch,
J.Chem.Soc., Dalton Trans., 1979, 506.

6. Oxidative-insertion Reactions of Zerovalent Nickel and Platinum Complexes with 1,7-Dicarba-closo-octaborane, 4,5-Dicarba-closo-nonaborane, and 1,6-Dicarba-closo-decaborane and Their C-Methyl Derivatives.
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8. Lower Rotational Barriers in Seven-Vertex than in Twelve-Vertex Carbaplatinaboranes: Synthesis, and Molecular and Crystal Structures of $[\text{closo-}1,1-(\text{Et}_3\text{P})_2-2,3-\text{Me}_2-1,2,3-\text{PtC}_2\text{B}_4\text{H}_4]$ and $[\text{closo-}1,1-(\text{Et}_3\text{P})_2-1,2,4-\text{PtC}_2\text{B}_4\text{H}_6]$.
by G.K. Barker, M. Green, F.G.A. Stone, and A.J. Welch,
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9. Stepwise Formation of Di- and Tri-platinum Complexes with Bridging Alkyne Ligands; Crystal Structure of $[\text{Pt}_3\{\mu-(\text{n}^2-\text{PhC}_2\text{Ph})\}_2(\text{PEt}_3)_4]$.
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by L.J. Farrugia, J.A.K. Howard, P. Mitrprachachon, F.G.A. Stone, and P. Woodward, J.Chem.Soc., Dalton Trans., 1981, 155.
11. Some Reactions of the Platinumtriosmium Complexes $[\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}(\text{PR}_3)]$ with Donor Molecules; X-Ray Crystal Structures of $[\text{Os}_3\text{Pt}(\mu\text{-H})_2(\text{CO})_{10}(\text{PPh}_3)_2]$ and $[\text{OsPt}_2(\text{CO})_5(\text{PPh}_3)_2(\mu_3\text{-MeC}_2\text{Me})]$.
by L.J. Farrugia, J.A.K. Howard, P. Mitrprachachon, F.G.A. Stone, and P. Woodward, J.Chem.Soc., Dalton Trans., 1981, 162.
12. Synthesis and X-Ray Crystal Structure of $[\text{NiOs}_3(\mu\text{-H})_2(\mu\text{-CO})_2(\text{CO})_8(\text{PPh}_3)_2]$ and $[\text{Os}_3\text{Rh}(\mu\text{-H})_2(\text{acac})(\text{CO})_{10}]$ (acac = acetylacetone).
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13. Synthesis and X-Ray Crystal Structure of $[\text{N}(\text{PPh}_3)_2][\text{Fe}_2\text{Pt}_2(\mu\text{-H})(\mu\text{-CO})_3(\text{CO})_5(\text{PPh}_3)_2]$, $[\text{Fe}_2\text{Pt}_2(\mu\text{-H})_2(\text{CO})_8(\text{PPh}_3)_2]$ and $[\text{Fe}_2\text{Pt}(\text{cyclo-C}_8\text{H}_{12})(\text{CO})_8]$.
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by R. Goddard, S.A.R. Knox, R.F.D. Stansfield, F.G.A. Stone, M.J. Winter, and P. Woodward, J.Chem.Soc., Dalton Trans., 1981, in press.

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